Electrical Properties of Evaporated Bismuth Films (II)

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Elektrische Eigenschaften von Verdampften Wismutfilms (II)

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Die elektrische spezifische Widerstände und Hallkoeffizienten wurden bei Temperatur von 77 bis 300 K für die mit Glas gekleidete Wismutfilms gemessen, die wurden über eine Glasscheibe bei Zimmertemperatur in Vakuum etwa 10^{-5} Torr verdampft. Die Temperaturabhängigkeit der Hallkoeffizienten für dünner Films mit die Dünnheit kleiner als 500 Å hat eine anomale Verhalten gezeigt ; die ein Minimumwert beim gewisse Kritischtemperatur T_c hat und die Temperatur T_c nimmt linieartig mit abnehmende Dünnheit ab. Qualitative Diskussion wird auf der Grund von die ordinäre " Size-Effekt" sowie die "Quantum-Size-Effekt" gegeben.

1. Introduction

In a previous paper,[1] some transport properties were reported on the evaporated Bi films such as the resistivity and magnetoresistance but no Hall coefficient. The electrical measurements were made by the two-terminal method with a conventional dc potentiometer. All the samples used, deposited on a slide-glass at room temperature, were not covered with any material, and were subjected to a little oxidation, as was seen from the change in the resistivity. The preliminary results were qualitatively understood by the ordinary size effect model.

For further understanding of the electrical properties of Bi films, the similar measurements have been carried out. But in the present experiment the four-terminal method is employed to measure the Hall effect and the samples are all covered with evaporated glass to prevent from oxidation of the film surface.

2. Experimental

Sample preparation was nearly the same as the previous study.[1] To prevent the Bi film surface from oxidation, additional evaporation of glass-wool was made on it right after the Bi deposition (Bi evaporation at a rate of 5-10 Å/sec). This coating procedure was found to be effective enough to obtain a stable Bi film, with a negligible change in the resistivity for a long period, and it was also

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confirmed that at least toward 77 K no mechanical breakdown was produced on cooling the sample.

The previous sample was, for simplicity, of the two-terminal structure, while in the present time the four-terminal structure was used for the Hall effect measurements, as shown schematically in Abb. 1. For this purpose, a thin phosphor bronze (0.2mm thick) was cut into a pattern by a spark-cutting machine as a mask for evaporation. Two types of the mask were prepared ; one for Bi and the other for electrode (Cu). The heater for Bi evaporation was a tantalum boat and that for Cu and glass was a tungusten wire. The electrical measurements were made by the dc potentiometric method.

3. Experimental Results

Abb. 2 shows the thickness dependence of the resistivity at room temperature, together with the previous data[1] of uncoated Bi films for comparison. In the latter case, the overall values are larger than the present results, because of contact resistance at the two electrodes and some formation of oxides. The resistivities of the present samples with thickness $t>1000\text{Å}$ approach to the bulk value ($\sim 1.2 \times 10^{-4}\Omega$-cm). Above 400Å, corresponding to the de Broglie wavelength, the resistivity ρ seems to oscillate with thickness t. One may think that this behavior is due to the quantum size effect, but this must further be confirmed by such as the magnetoresistance and Hall coefficient for various films.

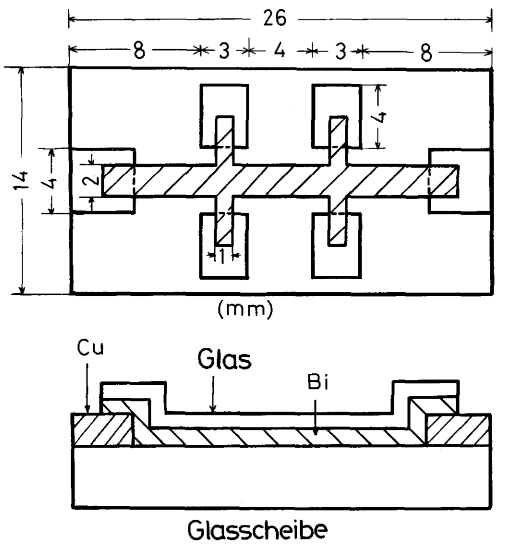

Abb. 1. Schematische Darstellung des mit dem Verdampfteglas gekleidete Wismutfilms.

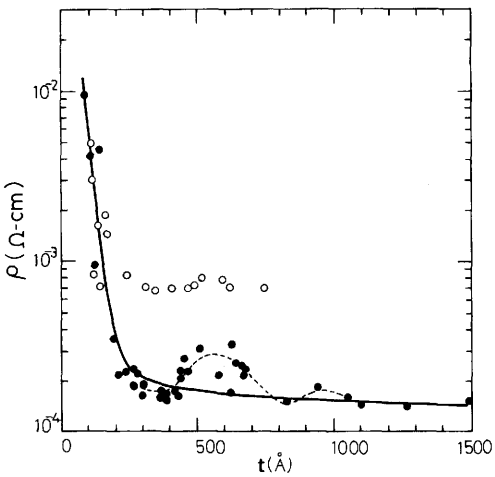

Abb. 2. Die Abhängigkeit der spezifischen Widerstände ρ von die Dünnheit t bei 300 K. Die punktierte Kurve zeigt eine wahrscheinliche Oszillation von ρ mit t. ○=frühere Arbeit,[1] ●=diese Arbeit.

The temperature dependence of the resistivity is shown in Abb. 3 for several films. The resistivity increases with lowering temperature and approaches to a constant, as reported so far.[1-3] Hoffman *et al.*[3] reported that for thicker films more than 2000 Å the resistivity minima appeared in the temperature range 100–300 K, and that the temperature at which the minima occurred shifted to a higher temperature side with the decrease in the thickness. They attributed the appearance of the minimum to a limiting of the carrier mean free path by boundary scattering. Furthermore, Garcia *et al.*[4] observed a small hysteresis and appearance of a small peak (*e.g.* at 116 K for $t=340$ Å) in the resistivity vs temperature curve for the films with $t<350$ Å ; these remained unexplained. In the present samples ($t \leq 1100$ Å), no such an anomaly were obtained ; the temperature was varied rather rough. More detailed studies are required to confirm these results.

The Hall coefficient R was estimated by the conventional way in the magnetic field up to 22 kG. The Hall voltages were approximately linear to the field strength H within the experimental errors, some samples showing a small field dependence. As in p-type Ge (the presence of light and heavy holes), the coefficient R in Bi may be expected to depend on H. At present no detailed studies are made for the Bi films. Abb. 4 demostrates the variation of the Hall coefficient measured at 15 kG with temperature. The following two behaviors of interest are to be noted from the figure. (1) For thicker films with $t>500$ Å, R increases with lowering temperature and becomes constant, as already reported.[2,3] (2) For thinner films with $t<500$ Å, the situation becomes quite different. The Hall coefficient, which shows a small maximum at 200~300 K for some samples, decreases with lowering temperature to a minimum value at a critical temperature T_c, accompanying the reversal of the sign from positive to negative, then the absolute value rises to a

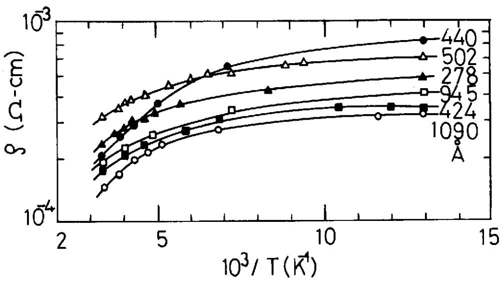

Abb. 3. Die Temperaturabhängigkeit der spezifischen Widerstände für verschiedenen Wismutfilms.

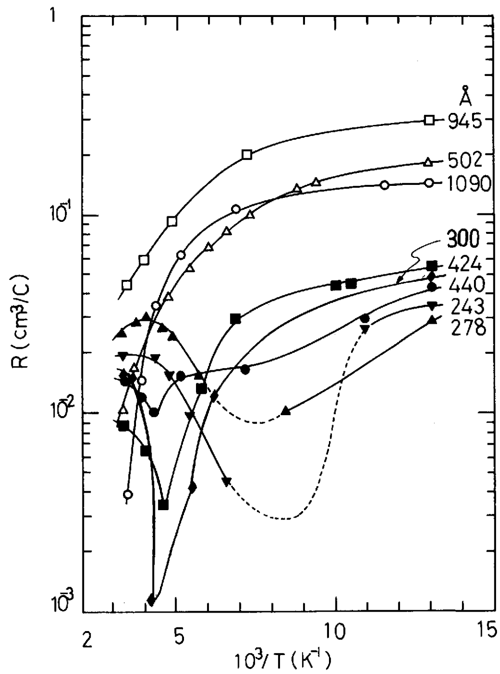

Abb. 4. Die Temperaturabhängigkeit der Hallkoeffizienten R.

constant at lower temperature side. The critical temperature T_c decreases with the decrease in the film thickness, as indicated in Abb. 5. These anomalous behaviors may correspond to the small anomaly in the resistivity vs temperature curve at 116 K for the film with $t=340$ Å found by Garcia *et al.*[4] We have not measured the resistivity anomaly in our samples, in particular around the critical temperature.

Since the Hall coefficient R shows anomalies and the resistivity changes monotonically with temperature, then the observed Hall mobility μ $(=R/\rho)$ shows a complicated temperature dependence, as shown in Abb. 6 ; different behavior between the thick film with $t>500$ Å and the thinner film with $t<500$ Å. The absolute values of μ are smaller than those of Sawatari *et al.*[2] For the thicker films, the T-dependence of μ is larger, $T^{-2\sim-3}$, compared with the usual lattice scattering mobility $\mu\sim T^{-3/2}$.

Finally, the magnetoresistance effect at two fixed temperature 77 and 300 K shows approximately the same behavior as the previous results.[1] It would also be of interest to measure it around T_c rather than the extreme temperatures (300 and 77 K). These studies are now in progress.

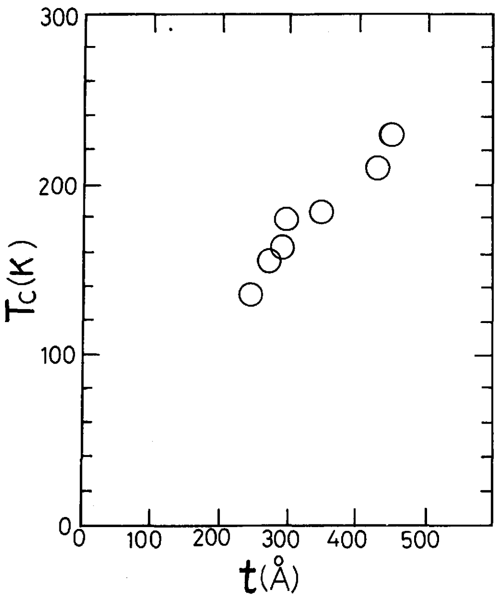

Abb. 5. Die Abhängigkeit der kritische Temperatur T_c von Filmsdünnheit, wobei die Hallkoeffizient der Minimumwert zeigt.

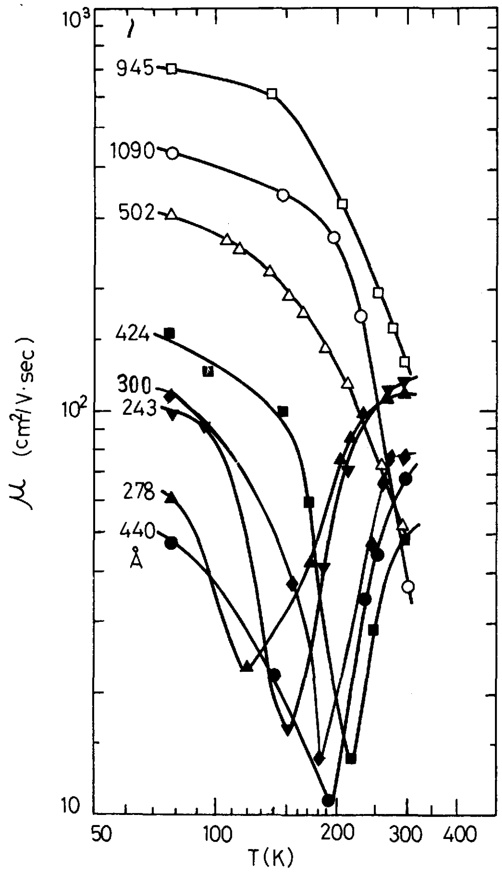

Abb. 6. Die Temperaturabhängigkeit der Hall-beweglichkeit μ $(=R/\rho)$.

4. Discussions

As we have discussed already,[1] the overall behavior of the thickness dependence of the resistivity can be well understood in terms of the ordinary size effect model. This effect is essentially due to the reduction of the carrier mean free path caused by a scattering at the boundary of the thin film. This scattering is partly elastic and in part inelastic in nature. The numerous expressions for the dependence of the resistivity on thickness have been presented by taking account of these scatterings ; in the paper of Hoffman *et al.*[3] historical references are well accumulated. As done before, let us compare the experimental results with the following equations,

$$\rho/\rho_0=1+0.4/\lambda, \qquad \rho_0/\rho=(3/4)\lambda(\ln\frac{1}{\lambda}+0.423), \cdots\cdots (1)$$

with $\lambda=t/l_0$,

where ρ is the resistivity of a film with thickness t, ρ_0 the bulk resistivity, and l_0 the bulk carrier mean free path. The calculated values are plotted in Abb. 7 by solid lines. For comparison, we cite the value of $\rho_0=1.14\times10^{-4}$ Ω-cm found by Hoffman *et al.*[3] As for the bulk mean free path l_0, it is not good to use the value $l_0=5900$ Å estimated by them, when the parameter of the elastic scattering is $p=0.56$. The best fit of the observed values with eq. (1) can be obtained when we use as l_0 the effective mean free path $l_e=500$ Å evaluated by Sawatari *et al.*[2] The discrepancy between the calculated and observed values for $\lambda<0.4$ may be due to the several causes such as island structure of the evaporated film, effect of adsorbed gasses, and formation of oxide film.

Let us consider next the interesting behavior of the Hall coefficient. The Hall coefficient R in isotropic material with two carriers, electron and hole, is expressed as, in a weak field approximation,

$$R=(p\mu_p^2-n\mu_n^2)/e(p\mu_p+n\mu_n)^2, \cdots\cdots (2)$$

where e is the electron charge, n and p the carrier concentration, μ_n and μ_p the

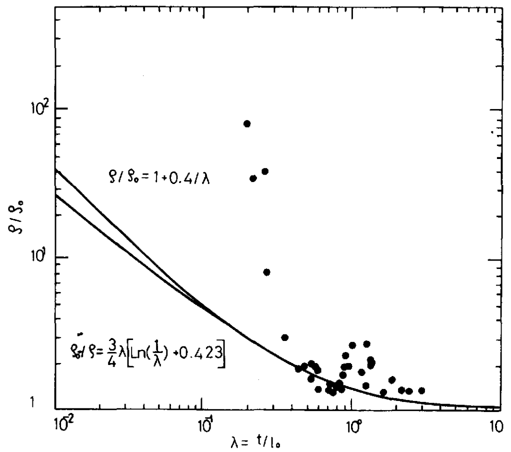

Abb. 7. Vergleich der normierte Dünnheitabhängigkeit der spezifischen Widerstände ρ/ρ_0 zwischen die nach Gl. (2) berechnete Kurve und die beobachtete Werte (s. Abb. 2), wo ρ_0 die Bulk-Widerstand $\rho_0=1.12\times10^{-4}$ Ω-cm und l_0 die Bulk-freie Weglänge ist. Der beobachte Verlauf stimmt mit die berecenete Kurve überein, wenn man benutzt die von Sawatari *et al.*[2] angegebenen effektive mittel freie Weglänge l_e (=500 Å) als l_0.

mobility, for electron and hole, respectively. Although this formula may not apply to Bi, which is highly anisotropic, it illustrates that the Hall coefficient may be very sensitive to small differences in the number of electrons and holes and to differences in the electron and hole mobilities. As shown in Abb. 4, the observed value of R for films with $t > 500$ Å changes monotonically, as have been reported so far, whereas for thinner films with $t < 500$ Å there appears a minimum at a critical temperature T_c. Though we cannot obtain the carrier concentration and mobilities for both carriers separately from the measured resistivity and Hall coefficient, the counter-balance may be realized that at T_c the numerator of eq. (2) vanishes. This condition, $p\mu_p^2 = n\mu_n^2$, depends on the film thickness as indicated in Abb. 5. If we assume $n = p$ for this condition, just as in the case of the bulk Bi, then we get $\mu_n = \mu_p$. However, this assumption is not reasonable, when we look at the magnitude of the effective masses of electrons and holes ;[5] $m_1^* = 0.0052$, $m_2^* = 1.21$, $m_3^* = 0.014$ for electron, and $m_1^* = 0.064 = m_2^*, m_3^* = 0.69$ for hole. That is,

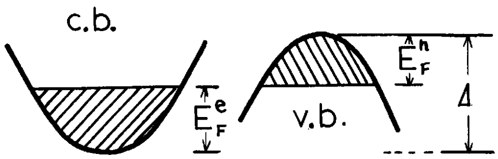

Abb. 8. Schematische Darstellung des Leitungsbands und Valenzbands in Halbmetall, wo-
E_F^h die zugehörigen Fermische Energie sind, und Δ die Energiedifferenz ist.

for films with $t < 500$ Å the relation $n = p$ is not necessarily satisfied.

We note furthermore that the overlapping of the electron and hole band Δ depends on the thickness, on the basis of the quantum size effect, and in a certain condition the energy difference Δ reduces to zero (see Abb. 8) ; transition from semimetal to semiconductor. In this case the condition $n = p$ is not necessarily fulfiled. In any way, the Hall coefficient minimum implies that approximately the condition $p\mu_p^2 = n\mu_n^2$ may be realized at the temperature T_c, which depends on thickness, but we cannot at present verify the condition independently. Thus it may be required to obtain the respective carrier concentration and mobility for electron and hole from additional informations such as,

i) magnetic field dependence of the Hall coefficient,

ii) cyclotron resonance, and

iii) helicon propagation.

We will report the measurement of i) later.

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Note added in proof

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